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COMBUSTION-CONDUCTOMETRIC DETERMINATION OF LESS THAN 10 P.P.M. CARBON IN TUNGSTEN

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ABSTRACT

The application of the combustion-conductometric method for the determination of carbon in highly pure tungsten suffers from two limitations. First, the smallest detectable quantity of carbon in the sample is limited by errors introduced by spurious amounts of carbon evolved from sources in the system other than the sample. Secondly, the accuracy of the method for refractory metals is unknown since quantitative calibration is based on recoveries of carbon from steel samples or organic compounds.

Studies of the control of these possible sources of error have resulted in establishing conditions whereby carbon concentrations of 4 p.p.m. may be determined in tungsten metal with a precision of ±12% and an estimated accuracy with ±15% relative to the true carbon concentration. These conditions appear to be directly applicable to other metals including Nb, Ta, Ti, Zr, Cr, and Cu and to Mo with minor modifications.

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Tungsten metal which has been processed by floating-zone refining commonly contains less than 10 p.p.m. of carbon by weight. The quantitative determination of carbon in this material is of interest since it affords a method for measuring the effectiveness of the purification process and also because carbon apparently has an appreciable effect on the mechanical properties of the metal (10). However, quantitative determination of the carbon in this low range has proven to be a difficult task with existing methods.

The combustion-conductometric technique has found wide application as a method of analysis for carbon in a variety of metals (1, 2, 4, 5, 7, 8, 11). This method has also been applied to refractory metals in the original or modified form. The primary steps in the method are: (1) the combustion or oxidation of the sample by inductive heating in oxygen, which converts carbon in the sample to carbon dioxide, and (2) the detection of the evolved carbon dioxide by measuring the change in electrical conductivity when carbon dioxide is reacted with a dilute solution of barium hydroxide. The change in conductivity is related to carbon content in the samples by calibration with standard samples of the material being analyzed. In the case of

refractory metals, standard samples are not available. It is, therefore, necessary to base calibrations on the recovery of carbon from National Bureau of Standards samples for carbon in steel or synthesized standards such as organic compounds in which the carbon content is precisely known. The validity of the carbon determination in tungsten is therefore uncertain because it is based on the assumption that carbon is quantitatively evolved from the sample under experimental conditions. A second limitation of the method is the inability of the detector to distinguish between the signal due to the carbon dioxide from the sample and that arising from sources other than the sample (i.e., the "blank"). The lower limit of detection for carbon in this procedure is determined by the variation of this "blank," which makes the precise determination of carbon below 10 p.p.m. particularly difficult.

The purposes of this investigation were to achieve improved precision at the lower carbon concentrations and, in addition, to prove the accuracy of the method when applied to refractory metals, particularly tungsten. The oxidation step was investigated, and a new combustion technique is recommended. The precision and accuracy are reported, and the resultant analytical procedure is outlined in detail.

EXPERIMENTAL

Effect of Additive Materials on the Blank

A major part of the blank arises from materials such as iron, tin, lead, and copper (1, 5, 7, 8), which are introduced into the crucible with the sample to promote coupling with the high-frequency field and to aid in

the formation of a less viscous mixture. In many cases the use of additive materials is highly desirable, if not essential, in achieving quantitative liberation of carbon from the sample metal (6). At concentrations as low as 10 p.p.m., however, the errors introduced by variable amounts of carbon contributed by the additive limit the precision of the method. Experiments were conducted to obtain definitive data on the limitation imposed by a variety of typical additives alone. The limitations of the instrument itself in this respect would be indicative of the ultimate detection limit for carbon by this procedure. Table I is a compilation of results from experiments for various additive materials. Each number in the line labeled "Total Blank" (γ of carbon) represents an average of 10 determinations made over a period of two days for materials of different lots. Determinations on iron chips were made after screening to reduce variation in replicate runs. In these experiments, only that material retained on 10 mesh was used. Results are also shown for commercially available tin granules and tin capsules and for low carbon, electrolytic iron. Finally, the apparatus blank was determined by heating a quartz-enclosed graphite susceptor (Laboratory Equipment Corp. No. 550-182) to approximately 1200° C to simulate heating of the sample. Data in the lines labeled "Total Blank" (γ of carbon) and "Standard Deviation" (γ of carbon) were obtained for an operation cycle consisting of 2 min. heating and 6 min. flushing. The data in these lines show the magnitude of the average blank and the statistical variation associated with these determinations. These values represent an undesirable signal at the detector, which tends to mask the detection of carbon recovered from a

sample such as high-purity tungsten. The values in the last line show the limits of detection in p.p.m. of carbon for the additives listed. These values were determined by arbitrarily establishing the limit at three times the standard deviation to represent the 95% confidence level. The last figure in this line also shows the results for a 2-grams sample because this is the minimum recommended weight for the direct combustion of tungsten under the conditions to be described later.

A conclusion drawn from the data is that a significant source of error in the determination at low carbon concentrations is the carbon content of the additive. Observations also indicated that the presence of iron in the crucible was unnecessary in achieving quantitative evolution of carbon from tungsten, since little or no intermetallic reaction occurs.

When iron chips were fused in an induction furnace in the presence of tungsten metal, it was found that unreacted tungsten chips were formed into an agglomerate apparently by the "stirring-effect" of the high-frequency field. This has been observed by other investigators such as Huber & Chase (8) who recommend the crushing and optical examination of the fused sample for unreacted metal. In the present work, it was found that rarely would a crushing procedure alone disclose the presence of unreacted tungsten. Careful sectioning of the crucibles, however, showed that in about 80% of the fusions the tungsten metal could be found intact. (Fig. 1 shows one such example.) It appeared that the elimination of all additives to the crucible by heating the sample directly would not only simplify the operation, but would be a major step toward achieving a reproducible blank and, therefore, a lower detection limit for carbon. The latter was achieved by optimizing conditions for completely oxidizing tungsten metal by direct-combustion.

Direct-Combustion of Tungsten by Induction Heating

The thermodynamics for oxide formation of tungsten and other refractory metals appear to make these metals especially adaptable to combustion methods. Although tungsten metal was readily converted to WO_3 in a resistance furnace, the time required for complete oxidation did not permit the attainment of as low a blank as was possible by rapid oxidation in an induction furnace.

Attempts to reduce the blank level by careful selection of fluxes with especially low carbon contents have been reported. Haymes and Oller (7) reduce contamination from this source by prefusing an electrolytic iron bath in a helium atmosphere. They suggest that the residual carbon under these conditions is liberated by combining with the oxygen in the iron to form CO_2. They were successful in reducing the residual carbon from the iron to a negligible amount. Their procedure requires slight modifications of the standard instruments and introduces an operation which would be unncessary if conditions for directly heating the specimen could be devised (e.g., as in an induction furnace).

In order to provide effective coupling between the high-frequency field and a tungsten sample without resorting to the use of an additive, it is necessary to consider the relationship between the physical form of the sample and some principles of induction heating. Determinations were most often required for metal rods of 1/8 to 1/4 in. diameter and for metal powders on the order of 200-mesh particle size. The small diameter and relatively small surface area of the rods were not conducive to efficient induction heating in the megacycle frequency range, which is

based on a "skin-effect." Fine powders, while advantageous from the standpoint of oxidation, provide a discontinuous path for high-frequency energy and thus are also ineffective in transferring the energy. A study of the effect of particle size on heating under these conditions showed that metal granules sized between 16 and 80 mesh could be coupled effectively. Once the oxidation of tungsten commenced, the metal was converted into a fused oxide mass by an exothermic reaction at temperatures above 1450° C.

While this procedure was satisfactory for coarse powders and solid metals which can be reduced in size, it was not amenable to fine powders (i.e., finer than 80 mesh). These fine powders will couple directly, however, if the particles are compacted to provide a more continuous path for the high-frequency field. It was found that extremely fine powders could be sufficiently compacted with a blunt ceramic tool and hand pressure. For the majority of as received powders, unfortunately, this procedure was not sufficiently reproducible. However, several alternate methods based on simple forms of a platinum susceptor have been successfully used for fine powders. Platinum foil placed in the bottom of the crucible and covered with metal powder provides sufficient heat to initiate the oxidation, which is then self-sustaining (3). Platinum squares as small as 0.003 in. thick and 1/8 by 1/8 in. have been used successfully. The platinum may be readily conditioned by heating in the induction furnace. A platinum disc, 1 in. in diameter and 1/32 in. thick, will similarly act as a susceptor when placed under and in good thermal contact with the crucible, which contains the powder. These discs are easily fabricated and can be used indefinitely.

By using the combustion procedures described herein for metal and powders, it was possible to reduce the blank to a level more favorable for the determination of less than 10 p.p.m. of carbon in tungsten.

Figure 2 demonstrates that the total instrumental and crucible blank under these conditions is essentially the same as that obtained by using the susceptor described previously. Sample weights from 2 to 8 grams. were oxidized directly in refractory crucibles, and the averages of multiple determinations were plotted against sample weight. The extrapolation of the plot passes through about 0.15 ohm, which when converted to μ of carbon with a calibration curve is in agreement with that obtained for the susceptor alone.

Quantitative Recovery of Carbon from High-Purity Tungsten

The accurate determination of carbon by the combustion-conductometric procedure requires consideration of two factors: (1) the calibration of the response of the conductivity cell to absolute amounts of carbon dioxide, and (2) the determination of the fraction of total carbon evolved from the sample under experimental conditions. The calibration of the conductivity cell may be accomplished in several ways. For example, standards for carbon in steel certified by the National Bureau of Standards can be readily used for this purpose (1, 2, 7, 11). Primary standard organic compounds, such as potassium acid phthalate, can also be used for calibration (9). As a matter of convenience, the latter was the approach used in this work. Although potassium acid phthalate is available commercially in tin capsules, the blank correction for carbon in tin may prove undesirable

at the lower concentrations of carbon (table I). Aqueous solutions of potassium acid phthalate containing 100 γ of carbon per milliliter were added directly to porous ceramic discs (Laboratory Equipment No. 528-42) and oven dried at 110° C for approximately 1 hr. The dried discs were placed on top of a quartz-enclosed graphite susceptor and inductively heated to an estimated 1000° C for 2 min. This was followed by a 6-min. flushing cycle, since it had been shown that this period was required for the signal at the detector to reach a maximum plateau. The calibration and precision obtained in this procedure is shown in Figure 3. The extrapolation to about 0.15 ohm again corresponds to the "blanks" obtained for the susceptor alone and is equivalent to approximately 2 p.p.m. of carbon for a sample weighing 2 grams.

These experiments based on the oxidation of potassium acid phthalate provide the basis for the calibration of the conductivity cell but do not disclose the degree of carbon recovery from a tungsten sample, which is necessary to place the determination on a quantitative basis. The validity of reporting carbon in tungsten based on recoveries from iron, steel, or organic compounds appeared to warrant further testing, since these procedures are based on the assumption that the carbon contents of the metal sample and the calibrating material are totally evolved. Recovery experiments were designed to assess the effectiveness of the evolution of trace amounts of carbon from tungsten metal, by means of the direct-combustion procedure, by doping samples with near-stoichiometric WC and W_2C. The carbides of tungsten were chosen because it appeared they would most nearly simulate the chemical nature of the carbon in tungsten metal. Analytical

data supplied by the vendor and that obtained on the carbides in this laboratory are shown in Table II. The data show that for gross amounts of tungsten carbides the deviation from the stoiciometric value was not significant for the purposes of the experiment. The stoichiometric value was therefore used in calculating quantities of carbon, since this places the quantification on a basis which is not dependent upon the combustion-gravimetric procedure used for determining the carbon contents of tungsten carbides. To facilitate weighing microgram amounts, the powdered carbides were blended with pure tungsten powder containing less than 10 p.p.m. of carbon to form a mix containing approximately 1% carbon by weight. The additional tungsten added to the crucible with the carbides was negligible and did not require a correction.

The experimental procedure consisted of adding a few milligrams of the WC-tungsten or W_2C-tungsten mixtures directly to a refractory crucible. The additive was then covered by 2 grams of the tungsten base-material, which was prepared from electron-beam-melted tungsten that produced a signal of 0.4 ohm for a 2 gram sample. Table III is a summary of recovery experiments for WC and W_2C. Data are shown for carbon recoveries from carbides in the presence of tungsten metal and oxidized by direct-combustion in a refractory crucible. Comparative data are also shown for small amounts of a standard sample of iron, designated by the National Bureau of Standards as 55e. The amount of carbon recovered in each of these experiments was compared to the data on potassium acid phthalate, and the percentage difference is shown. The recoveries from the carbides were consistently greater than those obtained for the organic compound or the standard iron sample. The

higher percentage deviation at the lower amounts of carbon suggested a constant systematic error, such as might be caused by errors in the blank corrections of the various experiments. The average deviations range from approximately +4 to +8 percent for additions of carbides representing from 24 to 96 γ of carbon. The relative deviations would be expected to be somewhat greater for the smaller amounts of carbon normally obtained from samples of pure tungsten. The accuracy of the procedure therefore for pure tungsten was estimated at ±15% relative, at a concentrational level of 5 p.p.m.. The agreement on the recoveries shown in Table III was satisfactory and showed that in the direct oxidation of tungsten metal and formation of fused oxide the liberation of carbon from the sample was virtually complete.

RECOMMENDED PROCEDURE

The pertinent procedural details are summarized in Table IV. Samples obtained as solid metal are crushed in a hardened steel mortar until the bulk of the material passes a 16-mesh screen and is retained on an 80-mesh screen. The small amount of material passing the fine screen is combined with the sample granules since carbon segregation may occur. A considerable amount of iron may be introduced into the sample during this operation and will result in high values for carbon if not completely removed. This is accomplished by digestion in 1:1 HCl followed by thorough rinsing with water and drying with ether. Approximately 4 g. (2 to 8 g. depending on carbon content) of the prepared sample is added to a crucible, which must be previously conditioned by heating in flowing oxygen at 900° C for 15 min..

After placing the sample in the induction furnace, pure oxygen is flushed through the furnace and conductivity cell for 2 min. to divest the system of CO_2, which may be picked up during the loading operation. The furnace is then energized for an 8-min. combustion cycle, although the formation of tungstic oxide is generally complete in 2 min. (as indicated by the plate current meter). The carbon dioxide formed during this combustion cycle is collected at the conductivity cell. Resistivity readings in equivalent ohms are taken at a selected period in the temperature cycle of the thermostatically controlled bath near the end of the collection period. (The instrument used in this work gave the most reproducible readings 60 sec. after completion of a "heat-on" cycle.) The instrument readings are converted to γ of carbon by using a potassium acid phthalate calibration curve. Since blanks for the calibration and tungsten procedures are the same, it is convenient to plot all values as uncorrected.

RESULTS

The results of precision studies on the tungsten base-material for two commonly used techniques (involving commercial or electrolytic iron additives) in addition to the direct-combustion technique are shown in Table V. The carbon content of this material was found to be approximately 3 p.p.m. by means of the recommended procedure. The iron additives used in these experiments were selected from the lots which gave the lowest standard deviation from the data in Table I, and the comparisons therefore are more typical of intra-laboratory precision. Thus, the method using electrolytic iron gave slightly better precision than did the direct-combustion method. A conclusion drawn from the data was that the method

employing selected electrolytic iron was comparable to the direct-combustion method with both falling in the range of values reported in Table I for the experiments on the additive alone. It is probable that the results for electrolytic iron would appear less favorable on an inter-laboratory basis, which may be inferred from the spread reported in Table I for the additive alone. Comparison of the data in Table V shows that the method is blank-limited, and the precision may be further improved by increasing sample weights; for example, up to 8 g. (Fig. 2) for the direct-combustion procedure.

The advantages of performing the determination by direct-combustion are further demonstrated in Figure 4. Carbon determinations were made on single-crystal tungsten rod by using both the direct-combustion and the iron-additive techniques. The data show that the direct-combustion procedure gives a more satisfactory representation of the carbon gradient along the rod. The method using direct-combustion permits determination of carbon in tungsten at concentrations of approximately 4 p.p.m. with a precision of ±12% and an estimated accuracy within ±15% relative to the true carbon concentration based on recoveries of tungsten carbides from tungsten metal.

GENERAL COMMENTS

The recommended procedure will provide quantitative results for the determination of carbon in tungsten below 10 p.p.m. within the limits stated. Instrumental reliability, however, may vary between laboratories. For this reason it is important to establish the limitations of a particular instrument.

Guidelines used in this investigation consist of two basic instrumental checks. The variation in conductivity of a $Ba(OH)_2$ solution subjected to a continuous flow of oxygen for a period of 1/2 hr. should not exceed 0.1 ohm. Occasionally, a continuous drift in the conductivity readings under these conditions has been encountered. A common cause for such a drift is the presence of liquid in the glass stem of either the reference or sensing electrode. This condition may arise due to a faulty seal between the glass and the platinum at the tip of the glass envelope and may be corrected by removing the liquid under vacuum and subsequently sealing the glass-platinum juncture with a bead of epoxide adhesive.

The procedure used in this investigation for conditioning the furnace prior to operation consists of heating until readings for an 8-min. period do not exceed 0.3 ohm for multiple determinations. The blank may be determined with a quartz-enclosed graphite susceptor or the platinum devices described previously.

Since this method is successful in determining the carbon content in tungsten, the extension of the direct-combustion method to metals such as molybdenum, tantalum, niobium, zirconium, titanium, chromium, and copper is also of interest. These metals will couple directly if the particle size is similar to that described for tungsten. For these more ductile metals it is often necessary to provide the proper size by cutting or shearing. In sheet form up to 1/16 in. in thickness, these metals couple and oxidize especially rapidly by placing a section in the bottom of the crucible with the sheet oriented perpendicular to the axis of the induction coil. Complete oxidation is observed for molybdenum only if the sublimation

of molybdic oxide is allowed to go to completion. It appears, therefore, that a special trapping device is desirable to prevent contamination of the conductometric system by the volatile oxide. Tantalum, niobium, zirconium, titanium, chromium, and copper undergo fusion of the oxides similar to tungsten. Preliminary recovery experiments using TaC and NbC in the metals indicate quantitative recovery of carbon under the conditions described for tungsten.

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TABLE I. - COMPARISON OF BLANK LEVELS WITH AND WITHOUT ADDITIVE

	Additive material										Series of apparatus blanks (direct combustion)
	Iron chips screened[b]				Tin granules[b], 1 gram		Tin capsules[b]		Electrolyte iron, 1 gram		
	Lot designation										
	1	2	3	4	5	5	6	6	7	7	
Total blank, μ of carbon	26.0	39.4	39.5	40.1	12.3	10.8	12.0	15.7	19.2	11.3	4.9 3.7 4.3 2.8
Standard deviation[a], μ of carbon	4.0	1.4	2.5	4.0	3.7	2.4	3.0	6.0	1.1	2.7	1.3 2.0 1.8 1.5
Limits of detection per gram sample ppm (range of 3s[a])	4.2 to 12.0				7.2 to 8.1		9.0 to 18.0		3.3 to 8.1		3.8 to 6 (1.7 to 3.0[c])

[a] $s = \sqrt{\frac{d^2}{N - 1}}$

[b] Laboratory Equipment Corp.

[c] Based on 2 gram sample.

TABLE II. - GRAVIMETRIC DETERMINATION OF CARBON IN WC AND W_2C

[Purity, 99.9%.]

Material	Total carbon, %		
	Stoichiometric	Vendor	NASA
W_2C	3.16	3.18	3.19
WC	6.14	6.1	5.98

TABLE III. - RECOVERY OF CARBON BASED ON POTASSIUM ACID PHTHALATE CALIBRATION

[Percent deviation of 0.1 ohm in blank correction: 7 at 30 γ of carbon, 2 at 90 γ of carbon.]

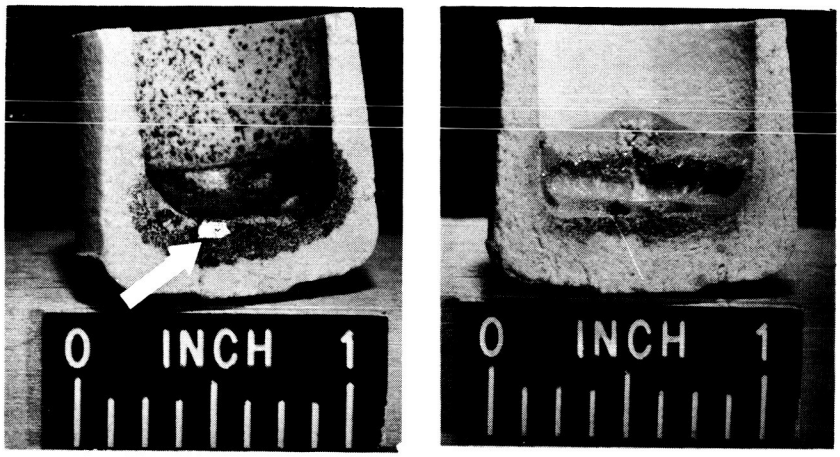
Sample	Added γ of carbon	Recovered % deviation from $KHC_8H_4O_4$	Sample	Added γ of carbon	Recovered % deviation from $KHC_8H_4O_4$
WC + 2g W	25	+28	W_2C + 2g W	24	+24
	25	0		26	+10
	28	+7		28	0
	26	+8		31	-3
	33	-12		35	0
	31	+38		42	+12
	28	+12		46	+2
	30	+3.3		53	+13
	30	-13.2		56	+11
	AV.	+8.0		64	+5
				AV.	+7.4
	46	+11			
	47	+11	Fe	30	+3.3
	57	-11	(NBS 55e)	30	+3.3
	67	+10		30	+15.0
	74	+5		30	+6.7
	74	+15		24	0
	80	-9		50	-6.0
	AV.	+4.6		90	-6.1
				90	+0.78
	96	+4.2		AV.	+2.1
	90	+7.2			
	95	+7.4			
	96	+2.1			
	93	+4.4			
	90	+2.7			
	AV	+4.3			

TABLE IV. - CONDITIONS FOR COMBUSTION-CONDUCTOMETRIC DETERMINATIONS OF CARBON IN TUNGSTEN

Instrumentation	Laboratory Equipment Corp. Model 515 (Furnace No. 521)
Crucible	Aluminum oxide Leco no. 528-25
Oxygen flow rate	250 to 300 ml/min.
Electrolyte	1 g/l. $Ba(OH)_2 \cdot 8H_2O$
Sample weight	~4 g. (2 to 8 g.)
Sample form	Powders - less than 80 mesh
	Granules - 16 to 80 mesh (and fines)
Susceptor	Pt foil or discs for powders
	None for granules
Calibration	W_2C+W mixture
	WC+W mixture
	Potassium acid phthalate
Combustion and collection time	8 min. total

TABLE V. - COMPARISON OF THE EFFECTS OF ADDITIVES ON THE DETERMINATION OF CARBON IN TUNGSTEN

Additive	Standard deviation, γ of carbon	Relative standard deviation, %	Carbon concentration, p.p.m.
Commercially prepared iron chip, 1 gram Fe + 1 gram W	2.3	55.0	4.2
Electrolytic iron, 1 gram Fe + 1 gram W	1.3	34.0	3.8
Direct combustion (no additive), 4 gram W	1.7	12.0	3.5



(a) FUSED TUNGSTEN PLUS IRON ADDITIVE

(b) FUSED TUNGSTEN (DIRECT — COMBUSTION)

C-66304

Figure 1. - Cross sections of refractory crucibles that have been used for the combustion of tungsten samples (with and without an iron additive). Note the agglomerate of unreacted tungsten in the sample (photograph (a)) containing the iron additive.

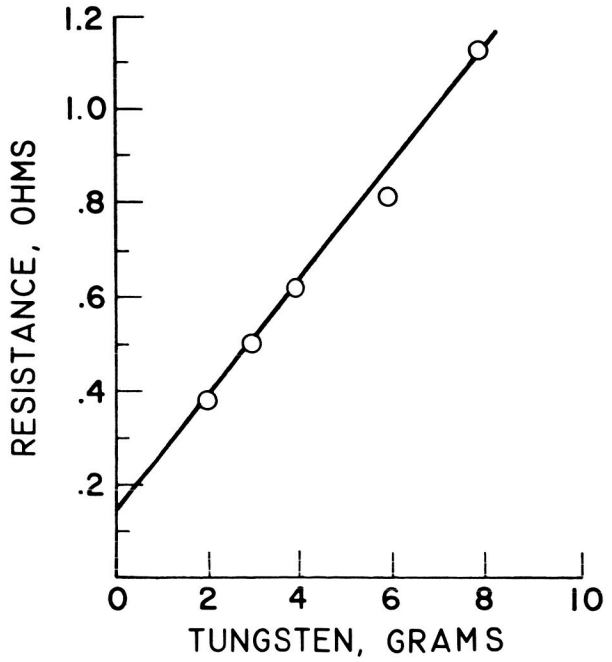


Figure 2. - Determination of blank by sample weight variation.

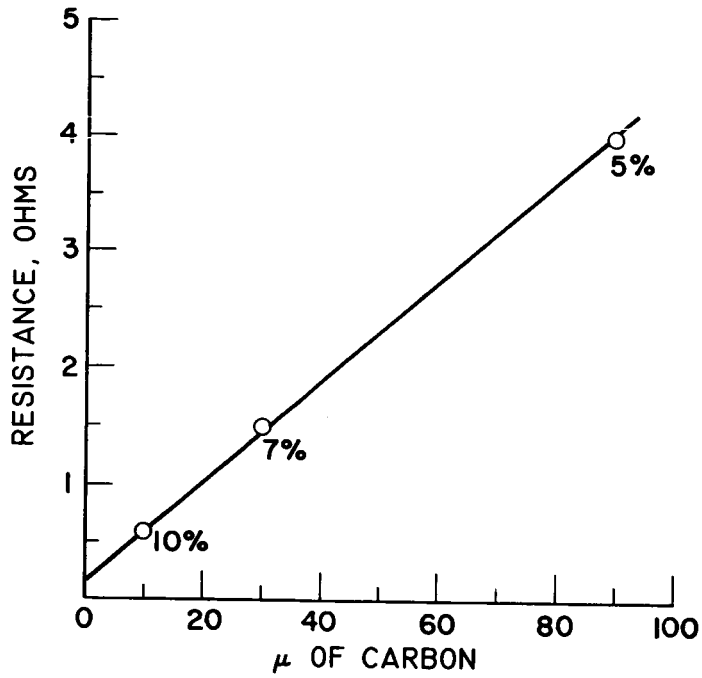


Figure 3. - Potassium acid phthlate calibration showing μ of carbon.

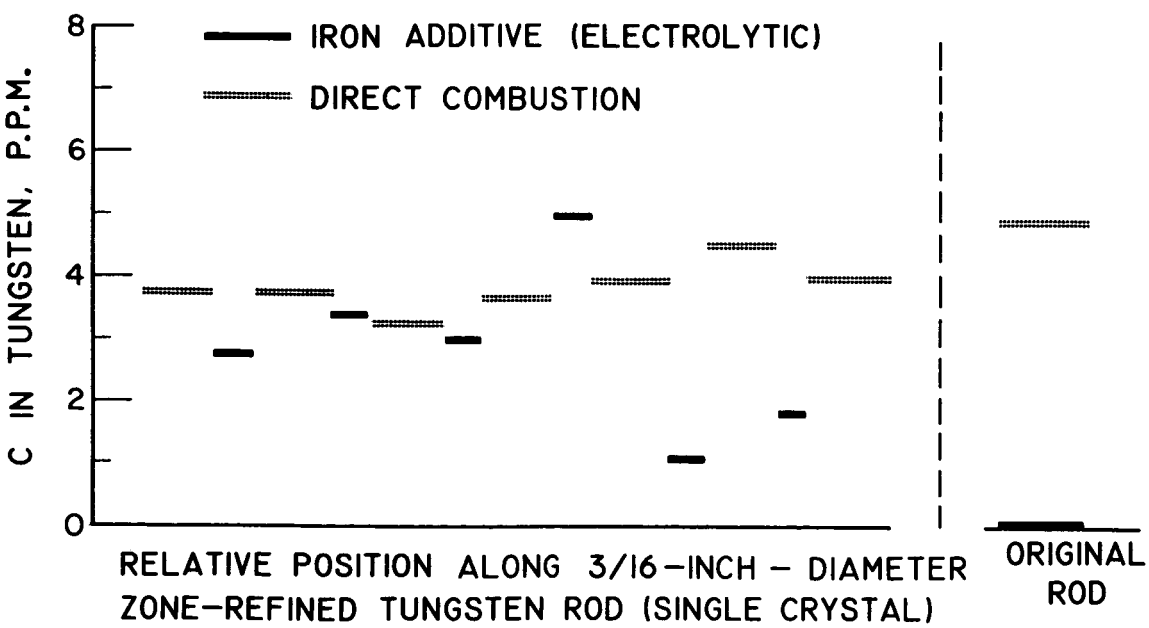


Figure 4. - Comparison of methods to determine the carbon gradient in zone-refined tungsten.